Spectral and time-resolved photoluminescence studies of Eu-doped GaN

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We report on spectral and time-resolved photoluminescence (PL) studies performed on Eu-doped GaN prepared by solid-source molecular-beam epitaxy. Using above-gap excitation, the integrated PL intensity of the main Eu^{3+} line at 622.3 nm ($^5D_0 \rightarrow {}^7F_2$ transition) decreased by nearly 90% between 14 K and room temperature. Using below-gap excitation, the integrated intensity of this line decreased by only $\sim 50\%$ for the same temperature range. In addition, the Eu^{3+} PL spectrum and decay dynamics changed significantly compared to above-gap excitation. These results suggest the existence of different Eu^{3+} centers with distinct optical properties. Photoluminescence excitation measurements revealed resonant intra-4*f* absorption lines of Eu^{3+} ions, as well as a broad excitation band centered at ~ 400 nm. This broad excitation band overlaps higher lying intra-4*f* Eu^{3+} energy levels, providing an efficient pathway for carrier-mediated excitation of Eu^{3+} ions in GaN. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1560557]

The visible and infrared light emissions from rare-earth-doped GaN (GaN:RE) are of significant current interest for applications in thin-film electroluminescence (EL) devices.[1–4] For achieving red light emission, the $^5D_0 \rightarrow {}^7F_2$ intra-4*f* transition of trivalent Eu^{3+} ions seems most promising. Intense red photoluminescence (PL) around 622 nm from GaN:Eu (as-grown and ion-implanted) has been reported from several research groups.[1–9] In addition, several EL device structures based on GaN:Eu have been demonstrated.[1–5] The optimization of present EL devices, however, requires a more detailed understanding of the incorporation, excitation, and emission properties of Eu^{3+} ions in the GaN host matrix.

Several studies have recently appeared focusing on the preparation and optical properties of GaN:Eu.[4–11] Based on the comparison to RE ions in other III–V semiconductors (e.g., InP:Yb,[12] GaAs:Er[13]), the most probable lattice location for Eu^{3+} ions in GaN are (substitutional) Ga sites, which have C_{3V} symmetry. However, significant differences in the Eu^{3+} PL properties have been observed depending on the material preparation. Monteiro *et al.*[7] studied Eu-implanted GaN and Eu *in situ* doped GaN grown by metal-organic chemical vapor deposition. They observed significant differences in the Eu^{3+} PL properties, including the number of emission lines associated with the $^5D_0 \rightarrow {}^7F_2$ transition. Based on optical spectroscopy and Rutherford backscattering studies, the authors concluded that the local symmetry of the Eu^{3+} ions has to be lower than C_{3V} symmetry.[7] Bang *et al.*[9] studied Eu-doped GaN prepared by gas-source molecular-beam epitaxy (MBE) and concluded, based on extended x-ray absorption fine-structure data, that Eu^{3+} occupies Ga sites with C_{3V} symmetry. It was also suggested that more than one local environment of Eu^{3+} ions may exist in the investigated GaN samples.

In this letter, we present PL results on GaN:Eu prepared by solid-source MBE, which provide spectroscopic evidence for the existence of different Eu^{3+} sites with distinct optical properties. Moreover, we report results of PL excitation (PLE) studies that identify the position of higher intra-4*f* Eu^{3+} energy levels as well as the existence of a broad defect band close to the conduction-band edge. This Eu-related defect level seems to play an important role in the efficient carrier-mediated excitation of Eu^{3+} ions in GaN.

The investigated GaN:Eu sample was prepared by solid-source MBE using a Riber MBE-32 system on a *p*-Si (111) substrate.[4] Solid sources were used to supply the Ga (7N purity) and Eu (3N purity) fluxes. A rf plasma source was used to generate atomic nitrogen. For the nitrogen plasma a rf power of 400 W and a N_2 flow rate of 1.5 sccm were employed. The Ga cell temperature ranged from 870 to 890 °C. A GaN buffer layer was first deposited for 10 min at a substrate temperature of 600 °C. For the main growth, the substrate temperature was ramped to 800 °C. The Eu cell temperature was 400 °C, resulting in an estimated Eu concentration of $\sim 10^{20}$–$10^{21}/\text{cm}^3$ (<2 at. %).

PL measurements were performed with an argon ion laser for above-gap (336.3–363.8 nm) and below-gap excitation (457.9 nm), respectively. For temperature-dependent PL studies the sample was mounted on the cold-finger of a two-stage, closed-cycle helium refrigerator. The visible emission was dispersed in a 1-m monochromator and detected with a thermoelectrically cooled photomulitiplier tube (PMT). PL lifetime measurements were performed with a third harmonic output of a pulsed Nd:YAG laser for above-gap excitation (355 nm). Below-gap excitation (~ 460 nm) was achieved using the output of an optical parametric oscillator (OPO)

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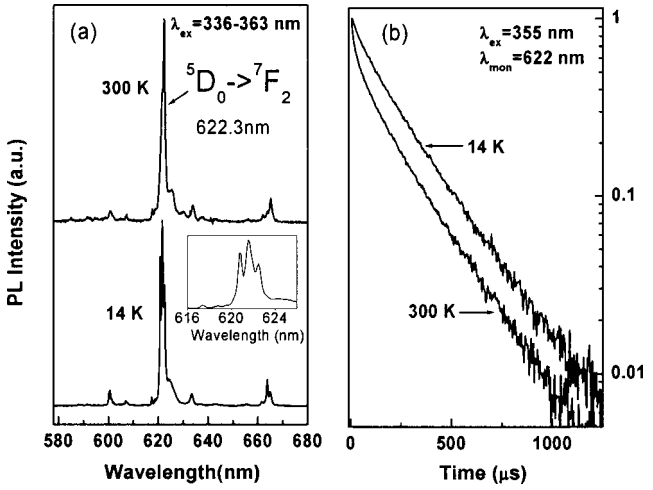

FIG. 1. (a) PL spectra of GaN:Eu under above-gap excitation (336–363 nm) at 14 and 300 K. (b) PL decay transients under above-gap excitation (355 nm) at 14 and 300 K. The inset in (a) shows the high-resolution spectrum in the region of the red Eu^{3+} line at 622.4 nm.

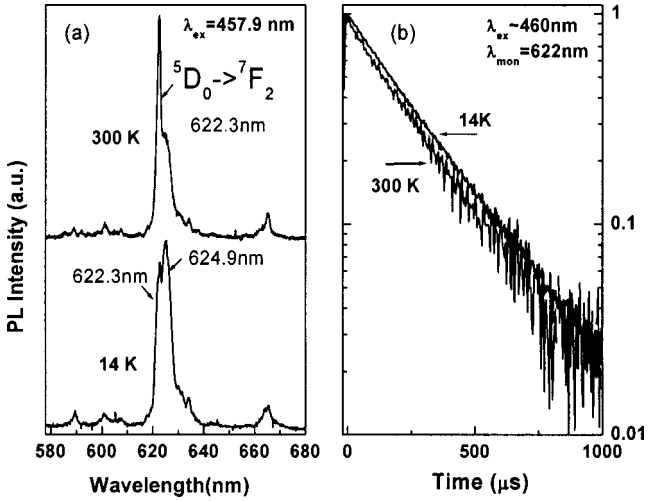

FIG. 2. (a) PL spectra of GaN:Eu under below-gap excitation (457.9 nm) at 14 and 300 K. (b) PL decay transients under below-gap excitation (460 nm) at 14 and 300 K.

system. The PL decay signals were detected by a PMT and averaged using a digitizing oscilloscope. The UV and visible output of a narrow-band ($\Delta\lambda \sim 0.1\ cm^{-1}$) OPO system were employed for PLE studies. The PLE spectrum was normalized to the pump energy of the excitation source.

High-resolution ($\Delta\lambda \sim 0.1$ nm) PL spectra of GaN:Eu at low (14 K) and room temperature under above-gap excitation are shown in Fig. 1(a). Characteristic intra-$4f$ Eu^{3+} emission lines were observed in the visible spectral region and were assigned in accordance with previous reports of Eu^{3+} ions in solid hosts.[14,15] The strongest Eu^{3+} emission line peaked at 622.3 nm and was attributed to the transition $^5D_0 \rightarrow {}^7F_2$. The full width half maximum (FWHM) linewidth of the 622.3 nm emission was determined to be ~ 1.6 nm at 300 K. This linewidth is less than half of the value reported by Li *et al.*[10] for GaN:Eu prepared by gas-source MBE on sapphire substrate, which indicates that the investigated sample is of higher crystalline quality and good uniformity. The inset in Fig. 1 shows that at 14 K, the red emission line splits into three main lines located at 620.8, 621.6, and 622.5 nm, and several weaker lines at shorter and longer wavelengths. For Eu^{3+} ions in C_{3V} site symmetry only three crystal-field levels are predicted for the $^5D_0 \rightarrow {}^7F_2$ transition.[15] The observation of more than three lines therefore suggests a local site symmetry lower than C_{3V}. An unambiguous assignment of the observed emission lines and Eu^{3+} site symmetry, however, is not possible because of the existence of different Eu^{3+} sites in GaN as will be discussed in the following. Moreover, it is possible that some emission lines arise from electron-phonon interactions and/or other impurities.[15]

The PL decay transients under-above gap excitation monitored at ~ 622 nm at 14 and 300 K are shown in Fig. 1(b). It can be noticed that the decay transients are slightly nonexponential with a fast initial decay component followed by a longer decaying component. Fitting the room-temperature transient to a double-exponential decay (inset equation) revealed that the fast decay component was $\sim 30\ \mu$s and the slow decay component had a value of $\sim 240\ \mu$s. Li *et al.* previously reported that GaN:Eu samples with Eu concentrations up to ~ 2.2 at. % do not show PL concentration quenching.[10] Therefore, energy transfer processes resulting in nonexponential decay behavior should be negligible in the investigated sample. Nonexponential decay transients have been observed previously for other RE-doped semiconductors (e.g., GaN:Er,[16,17] AlN:Er,[18] GaAs:Er,[19] Si:Er[20]) and were attributed to the existence of different Er^{3+} sites with distinct decay channels.

Direct evidence for the existence of different Eu^{3+} sites was obtained from PL measurements using below-gap excitation. Near resonant intra-$4f$ Eu^{3+} excitation was carried out using the 457.9-nm output of an argon-ion laser. The spectral resolution in these measurements was only ~ 0.8 nm because of the weaker signal strength compared to above-gap excitation. The low-temperature PL spectrum revealed significant spectral differences compared to above-gap excitation [Fig. 2(a)]. It can be noticed that the shoulder located at ~ 624.9 nm has gained significant intensity relative to the main line at 622.3 nm originating from the $^5D_0 \rightarrow {}^7F_2$ transition. Moreover, the Eu^{3+} decay transients at 14 and 300 K were found to be single exponential and nearly independent of temperature [Fig. 2(b)]. The PL decay time was determined to be $\sim 240\ \mu$s, which matched the slow-decaying component identified in the above-gap transients shown in Fig. 1(b). The data indicate that under below-gap excitation only a subset of the Eu^{3+} ions are selectively excited.

In Fig. 3 are shown the integrated PL intensity and lifetime of the red Eu^{3+} emission. Using above-gap excitation, the integrated PL was quenched by $\sim 90\%$ as the temperature increased from 14 to 300 K. The average PL lifetime (defined as the area under the decay transients), decreased only slightly ($\sim 10\%$) for the same temperature range indicating that nonradiative decay processes only weakly affect the Eu^{3+} PL. Therefore, the strong Eu^{3+} PL quenching under above-gap excitation is attributed to the temperature dependence of the carrier-mediated energy transfer process between the Eu^{3+} ions and the GaN host. Using below-gap pumping, the integrated Eu^{3+} PL intensity decreased by only a factor of 2 between 14 and 300 K, and the PL lifetime was nearly constant. Therefore, the weak Eu^{3+} PL quenching

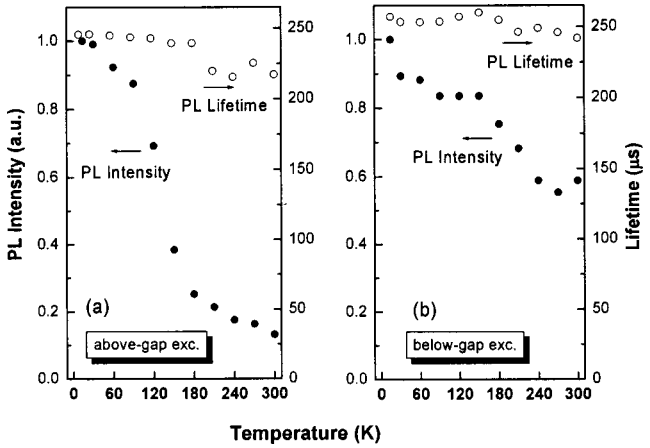

FIG. 3. Temperature dependence of the integrated PL intensity (solid circles) and PL lifetime (open circles) of GaN:Eu under (a) above-gap and (b) below-gap excitation.

with below-gap excitation is due to a slight change in the excitation efficiency.[21]

More information on the Eu^{3+} excitation and de-excitation properties was derived from PLE measurements depicted in Fig. 4. The PLE spectrum allows the identification of several intra-$4f$ Eu^{3+} absorption lines located at ~412 nm ($^7F_0 \rightarrow {}^5D_3$), ~471.2 nm ($^7F_0 \rightarrow {}^5D_2$), ~533.7 nm ($^7F_0 \rightarrow {}^5D_1$), ~543.5 nm ($^7F_1 \rightarrow {}^5D_1$), and ~590 nm ($^7F_1 \rightarrow {}^5D_0$). A broad excitation band (FWHM~21 nm) was centered at ~400 nm (3.1 eV), which overlapped the higher-lying Eu^{3+} transition $^7F_0 \rightarrow {}^5D_3$. This band also overlaps the transition $^7F_0 \rightarrow {}^5L_6$.[14] Based on Fourier transform infrared measurements, Li *et al.*[10] recently reported a Eu-related defect level at 0.37 eV below the conduction band of GaN. Such a band closely matches the observed broad PLE band identified in Fig. 4. The PLE results for GaN:Eu suggest that the broad-defect level provides an efficient pathway for the carrier-mediated energy transfer between Eu^{3+} ions and the GaN host. It is interesting to note that a defect level

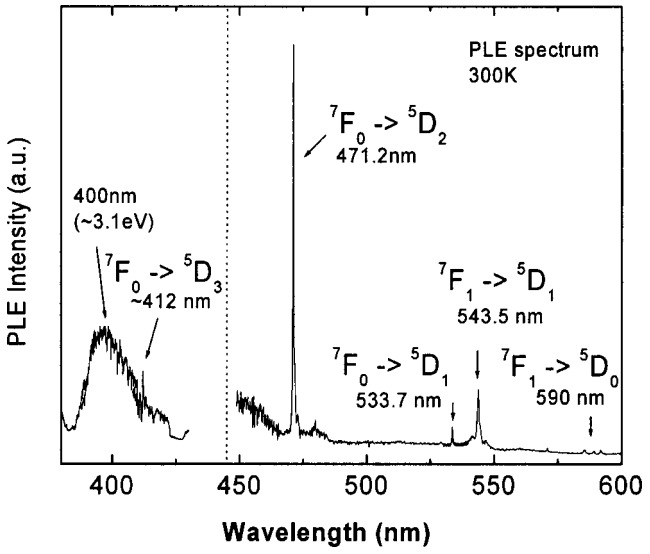

FIG. 4. PLE spectrum at 300 K of GaN:Eu monitored at 622.3 nm. The dotted line indicates a break in the relative PLE signal because of a change in the OPO excitation source.

~400 nm was also observed in the PLE spectra of Er-implanted GaN.[17] Previously, RE-related trap levels have been proposed as a means to explain the excitation of intra-$4f$ transitions of RE ions in other III–V semiconductors, e.g., InP:Yb[12] and GaAs:Er.[13]

In summary, we have obtained spectroscopic results of the optical properties of Eu^{3+} ions in GaN:Eu prepared by solid-source MBE. Wavelength-dependent PL studies revealed the existence of different Eu^{3+} centers with distinct optical properties. PLE measurements have provided evidence for a defect-related trap level that may be involved in the energy transfer between the GaN host and the Eu^{3+} ions. It seems likely that the carrier-mediated excitation of RE ions in III-nitrides can be optimized through careful manipulation of the RE-related defect levels and higher lying intra-$4f$ RE transitions. This manipulation could possibly be achieved through band-gap engineering of the host or through co-doping with sensitizer ions. Further comparative PLE studies of other RE-doped III-nitrides are currently in progress to support the defect-mediated excitation model.

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